



## Imaging microscale fluid dynamics

Flow in microchannels plays a key role in micro-electromechanical systems as applied to wafer scale analytical instruments (*CRF News* 19:4). Much of the knowledge about these flows is based on measurements of macroscopic observables such as total flow rates or pressure drops. Studies at microscale have relied on visualizing the flow using tracer dyes. This method is limited by the dye-injection process, by flow history, and by diffusional blurring. Phil Paul and Dave Rakestraw have developed a new laser-based tool for imaging microscale flows. Working with Postdoctoral Associate Mike Garguilo, they have applied this instrument to study liquid flows in microchannels.

The technique is based on optically writing a known pattern into the flow and then optically interrogating the flow at a later time to observe how this pattern is transported. The 'write' step is performed by 'uncaging' a laser dye that has been added in trace quantities to the flow. This is done by illuminating the flow with a thin sheet of pulsed laser light at 355 nm. The dye is initially in a 'caged' state that will not fluoresce. UV photolysis irreversibly modifies the caged dye to one that can fluoresce. At selected time delays following 'uncaging,' the flow is flood-illuminated with pulsed laser light at 473 nm to excite the uncaged dye. The resulting fluorescence pattern is imaged onto a CCD array camera. This is still a dye tracer method; however the 'injection' is performed optically, which allows high-contrast images to be obtained anywhere in the flow system. The entire system is built in the form of a microscope (see Figure 1).

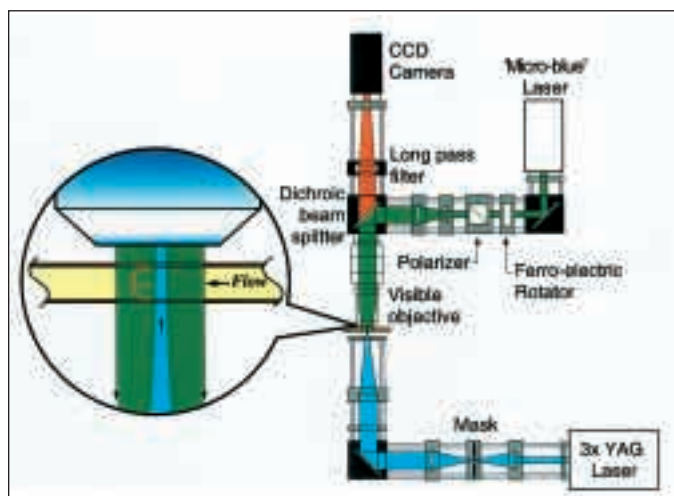


Figure 1: Schematic of the imaging instrument.

Figure 2a shows an image of a pressure-driven parabolic pipe flow taken some 198 ms following the uncaging event. The displacement of the dye reveals the largest velocity on centerline and an essentially stagnant flow near the walls. In this case a caged fluorescein dextran dye (MW=10,000) was used to reduce blurring by diffusion.

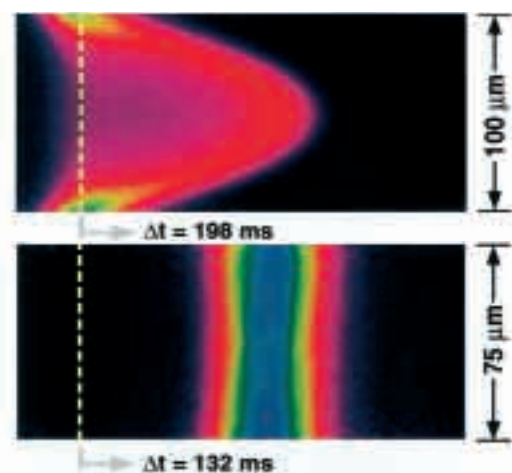


Figure 2: Single pulse images of: (a) pressure-driven flow in a 100  $\mu\text{m}$  i.d. capillary at 198 ms after uncaging. Centerline velocity of 0.71 mm/sec; and (b) EK-driven flow in a 75  $\mu\text{m}$  i.d. capillary at 132 ms after uncaging. Centerline velocity of 0.68 mm/sec obtained at 200 V/cm.

When the capillary is filled with an electrolytic solution, a charged double layer forms at the liquid-solid interface. An applied axial DC electric field produces a body force on the net charge. This force is viscously coupled to the rest of the neutral fluid creating an electrokinetic (EK) flow. Figure 2b shows an image of an EK-driven flow taken some 132 ms following the uncaging event. In this case a caged rhodamine dye (MW=560) was used. The fluid is an 80:20 mixture of acetonitrile and water buffered with 5 mM aqueous TRIS. A plug flow is observed. The uncaged dye spreads axially in time owing to simple diffusion.

The imaging tool is currently being applied to study flows in more complicated planar geometries that are being fabricated using semiconductor manufacturing techniques. This work is aimed at identifying and characterizing pressure- and EK-driven flow phenomena as a basis to develop scaling laws and for validation of micro-flow simulations. The resulting engineering models will have broad applications ranging from the design of wafer-scale analytical instruments to the development of miniature hydraulic and thermofluid systems.

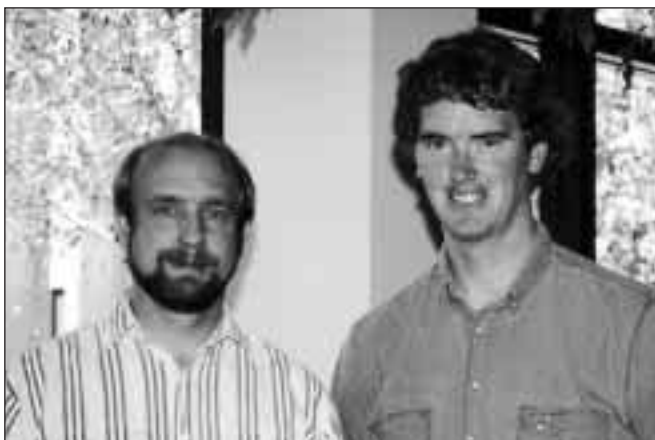


Professor Stewart Cant (left) from the University of Cambridge, participated in the Combustion Modeling Workshop this summer and collaborated with Jackie Chen on developing turbulent premixed combustion models to describe multi-step hydrocarbon flames. Stewart used recent turbulent premixed methane-air direct numerical simulation data by Jackie to evaluate various terms in the Bray-Moss-Libby model.

## Combustion Research Bulletin added to website

A new feature of the CRF WorldWideWeb site is the Combustion Research Bulletin (<http://www.ca.sandia.gov/CRF/Publications/CRB/CRB.html>). The Bulletin is compiled by Keith Schofield of ChemData Research, Santa Barbara, CA under a contract with Sandia and is sponsored by the Office of Basic Energy Sciences, Department of Energy. The Bulletin consists of technical abstracts, technical meeting announcements, and current bibliography relevant to fundamental combustion gathered from worldwide sources; it is updated bimonthly.

The CRB was started in 1980 and since then has included some 720,000 references culled from about 640 reference titles. The Bulletin now contains about 750 references per issue. The CRF has been happy to cooperate in this effort by handling printing and distribution – and now adding it to the CRF website.



Peter Powers (right) recently completed his postdoctoral assignment in the Remote Sensing Group, working with Tom Kulp (left) on infrared sensing projects. Peter has taken a position as Professor at the University of Dayton, where he will teach physics and continue his work in developing new nonlinear laser sources.

## Adams and Bastress Awards given

The presentation of these two prestigious CRF awards was made on August 26. Phil Paul was the recipient of the O.W. Adams Award and Mark Allendorf received the E.K. Bastress Award. For more information, see "What's Hot at the CRF" for September on the website,

[www.ca.sandia.gov/CRF](http://www.ca.sandia.gov/CRF).



Perry P. Yaney (right), Professor of physics and electro-optics from the University of Dayton, spent a sabbatical leave at the CRF working with Roger Farrow to develop a short-pulse, tunable UV laser for a new user laboratory. Through fine tuning of the laser wavelength near 281 nm, the 80-ps laser pulses provided high-quality degenerate four-wave mixing spectra of OH in a flame.

## Combustion Modeling Workshop held in CRF

Fundamental issues in predictive combustion modeling were discussed at a workshop held in the CRF August 18-22. Opportunities presented by new CRF Phase II experimental capabilities and the advent of teraflop computing were also explored. The workshop and the associated summer visiting research program in combustion modeling and simulation were facilitated by the recent completion of a new office wing, part of the CRF Phase II construction project. Over 60 participants enjoyed an active program of presentations and discussion that was complemented by two evening social events.

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## Cofiring contributes to global warming solution

Sandia researchers are addressing cofiring of biomass and coal as part of the solution to global warming. This collaborative project involves Allen Robinson, Larry Baxter, Helle Junker (Elsamprojekt, Denmark), Gian Sclipa, the National Renewable Energy Laboratory, and the Federal Energy Technology Center. The U.S. involvement is being jointly sponsored by DOE Office of Fossil Energy and Office of Energy Efficiency and Renewable Energy. The objectives of the project are to demonstrate that 10-15% biomass can be cofired with coal on a long-term basis and to evaluate combustion characteristics of candidate fuels.

Low-cost options for biomass cofiring involve residual materials including (a) scrap wood or sawdust from mills, pallets, and demolition sites; (b) crop residues such as prunings and straw; and (c) nonrecyclable paper and similar underutilized resources. Use of such materials as fuels prevents their open field combustion or disposal in landfills. The  $\text{CO}_2$  generated during combustion of such materials is reincorporated in new growth, resulting in essentially no net  $\text{CO}_2$  generation if properly managed.

The advantages of cofiring compared to other  $\text{CO}_2$  reduction schemes are illustrated in Figure 1, where cofiring is compared to increased efficiency in terms of  $\text{CO}_2$  generation. For example, firing biomass at a level of 20% of the total heat input to a power generation system is equivalent to increasing efficiency of the fossil-fuel-only power plant by 25% or an efficiency ratio of 1.25.

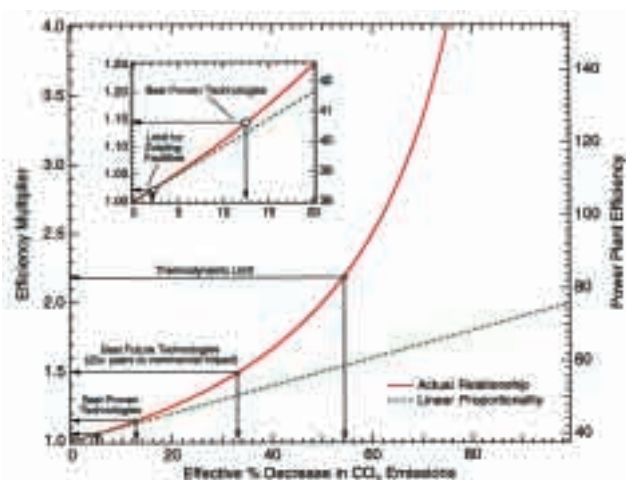


Figure 1. Biomass cofiring compared to increased efficiency in terms of  $\text{CO}_2$  reduction. The curved line indicates the efficiency increase required (left ordinate) to achieve the same result in terms of greenhouse gas emissions as is achieved at a given level of cofiring biomass with coal (abscissa) with no change in efficiency.

Biomass cofiring is not without technological challenges. The project at Sandia (Figure 2) addresses the most severe of the combustion-related issues. These include ash deposition, corrosion,  $\text{NO}_x$  emissions, and carbon burnout. Many biomass fuels are high in total ash and in alkali and chlorine relative to coal, portending issues related to ash management and corrosion. Most

biomass fuels of commercial significance contain less nitrogen and essentially all contain less sulfur than coal, leading to generally lower  $\text{NO}_x$  and  $\text{SO}_x$  emissions.

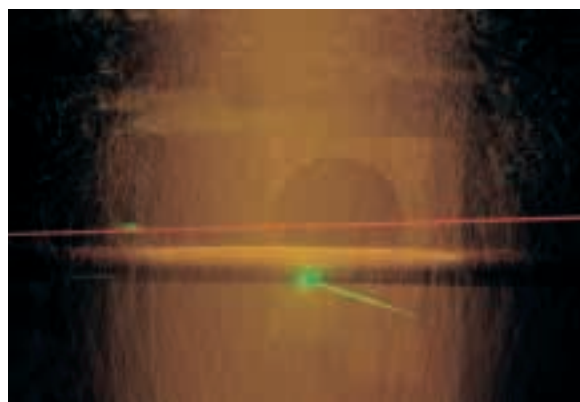


Figure 2. Photograph of the test section of Sandia's Multifuel Combustor (MFC) during experimentation using several optically based diagnostics. The laser lines represent some of the optical diagnostics used *in situ* to measure surface temperature and composition, deposit thickness, particle velocity and size, and similar variables in the MFC.

All of these technological issues are addressed in the research program. For example, Figure 3 illustrates issues related to corrosion and deposit properties. The mechanisms giving rise to this trend are associated with alkali chlorides (derived primarily from the biomass) combining with sulfur (derived primarily from the coal) to form alkali sulfates on heat transfer surfaces.

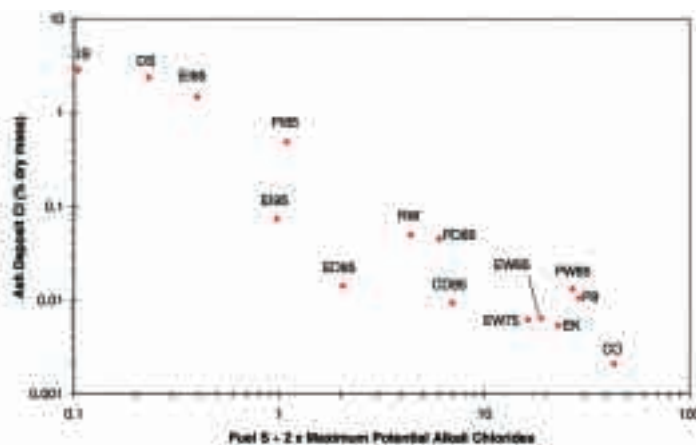



Figure 3. Ash deposit chlorine concentration as a function of fuel chlorine and sulfur concentrations. Chlorine concentration in the deposit drops rapidly (note logarithmic scales) as the ratio of sulfur to alkali chloride in the fuel increases. Letters designate various fuels and fuel blends tested in the MFC.

This research leads to cofiring guidelines relating to fuel selections, fuel preparation requirements, and maintenance schedules. Articulation of these guidelines will be the major focus of the research over the next few months. 



# Laser-induced fluorescence spectroscopy of the HCCO radical

Lori Brock and Eric Rohlffing, in collaboration with Daniel Neumark and Ryan Bise (University of California, Berkeley) and Bernhard Mischler (PSI, Switzerland), have observed the first laser-induced fluorescence (LIF) spectrum of the ketenyl radical (HCCO).

The ketenyl radical is an important intermediate in hydrocarbon combustion and is formed in flames principally by the reaction of oxygen atoms with acetylene. The characterization of the spectroscopy and dynamics of HCCO provides fundamental data that make it possible to test its potential as a molecular marker in combustion systems. LIF is utilized for this task because of its high sensitivity and its applicability to combustion systems and chemical kinetics environments.

An example of the jet-cooled LIF spectrum of HCCO is shown in Figure 1. Similar spectra are obtained for the isotopically substituted radical DCCO. A rotationally resolved spectrum of the vibronic origin band of DCCO, obtained by using a single-longitudinal mode optical parametric oscillator/amplifier system, is shown in Figure 2.

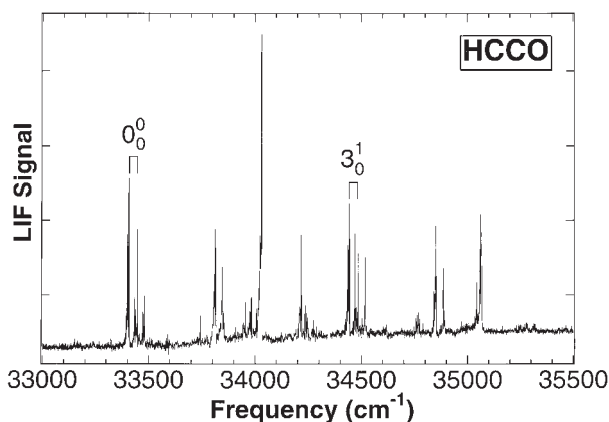


Figure 1. An LIF survey spectrum of the  $\tilde{B}^2\Pi - \tilde{X}^2A''$  band system of jet-cooled HCCO. A series of vibronic bands is observed, originating at  $33,424\text{ cm}^{-1}$ . At higher energies the LIF spectrum breaks off sharply due to a rapid increase in the rate of predissociation.

The spectroscopy of ketenyl is intrinsically interesting because the ground state,  $\tilde{X}^2A''$ , is bent and the observed excited state,  $\tilde{B}^2\Pi$ , is linear but subject to Renner-Teller

vibronic coupling via the two bending vibrations. Analysis of the spectra provides fundamental information about the  $\tilde{B}$  state vibrational frequencies, spin-orbit splitting and Renner parameters for both HCCO and DCCO. The rovibronic spectra may yield the geometry (bond lengths and angles) of the radical in both the bent ground state and linear excited state. These spectroscopic constants can then be compared with the results of *ab initio* calculations.

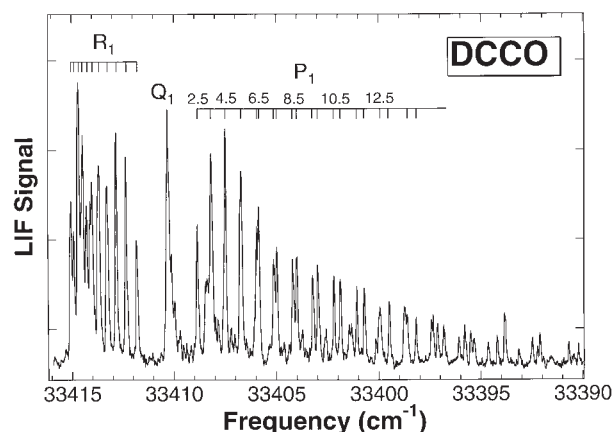


Figure 2. Rotational structure of the  $F_1 - F_1$  component of the DCCO  $\tilde{B}^2\Pi (K'=1) - \tilde{X}^2A'' (K''=1)$  origin band. Rotational labels are appropriate to Hund's case (a) coupling.

Lori and co-workers have measured the fluorescence decay for the HCCO origin band. From a fit to this decay using a convolution of the excitation function and an exponential, they can establish that the lifetime of the vibrationless level of the  $\tilde{B}$  state must be less than 1 ns and provide an estimate of the quantum yield of fluorescence of  $10^{-3}$ .

Although the quantum yield is small, LIF may still be a useful diagnostic for HCCO in some flames or in kinetics experiments. Further studies to characterize the spectroscopy and dynamics of the ketenyl radical using other techniques (dispersed fluorescence, stimulated emission pumping, and resonant enhanced multiphoton ionization) are currently underway.

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